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RESEARCH ON LOW DENSITY
THERMAL INSULATION MATERIALS
FOR USE ABOVE 3000°F
Quarterly Status Report
Contract NASw-884
National Beryllia Corporation
Haskell, New Jersey

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Quarterly Status Report
for the Period January 1 through March 31, 1964

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ABSTRACT

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Composite refractory materials for use as high temperature thermal insulation are being developed and evaluated. The mechanism under investigation is the attenuation of the radiation component of thermal conductivity by the incorporation of radiation barrier phases into a foamed ceramic matrix.

Specimens containing metallic tungsten or molybdenum thermal radiation barrier phases have been shown to be superior thermal insulators compared with unimpregnated ceramic foams. Thermal conductivity calculations in a 3/8" long gauge section, 1/8" from the heat source do not reflect this lower value. A multiple gauge section technique in which four gauge sections each 1/8" long, extending from the hot face of the specimen to a region 1/2" removed has been developed. Preliminary measurements employing this technique indicate that the radiation component is attenuated primarily in a skin region of probably less than 1/4". Further testing is required.

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(1) INTRODUCTION

This is the first quarterly report of Contract NASw-884 on the subject, "Research on Low Density Thermal Insulation Materials for Use above 3000°F". This program is a continuation of work performed on Contract NASr-99 which was conducted for seven quarters from April, 1962, through December, 1963.

1.1 Purpose of the Program

Low-density foamed ceramic thermal insulation rapidly loses efficiency above 2400°F due to the transfer of heat through the pores by thermal radiation. The purpose of this program is to study the reduction of this radiation or photon contribution to the thermal conductivity by the incorporation of a thermal radiation barrier phase into a low-density refractory structure. Mechanisms such as absorption and re-radiation by imbedded particles, scattering by incorporated phases and reflection by metallic foil radiation barriers are being investigated and evaluated.

1.2 Phases of the Program

The goals of this program are being achieved through the pursuit of the three phases described briefly below with details of the progress made during this quarter discussed in Section II.

Phase I - Technical Review

Review of previous high temperature heat transfer work, essentially completed during the first quarter, has been continued at a sufficient level of effort to keep abreast of the rapidly changing technology.

Phase II - Materials Formulation

The major effort of the program is concerned with the fabrication of low-density, low thermal conductivity materials. Light weight pure oxide ceramic matrices have been developed and impregnated with various volume percentages of potential radiation shielding phases introduced by a variety of techniques. Specimens of ceramic oxides whose thermal conductivity have been previously reported have also been prepared for calibration and equipment checkout purposes.

Phase III - Experimental Measurements

Evaluation of the thermal radiation barrier concept is being conducted in this phase of the program. A high temperature thermal conductivity test cell, capable of maintaining under steady conditions, specimen hot face temperatures of 4500°F and above has been fabricated and calibrated. Measurement of the apparent total conductivity of the ceramic foam composite test samples is in progress.

(2) DISCUSSION

2.1 Phase I - Technical Review

The "Symposium on the Thermal Radiation of Solids" was attended in San Francisco March 3 to 6, 1964. Many fine papers on the emittance characteristics of ceramics and pure oxide materials were reviewed and discussed. Of particular interest was a paper by Prof. E. M. Sparrow of the University of Minnesota concerning the radiation properties of cavities. (1) In subsequent communication with Prof. Sparrow some data from a computer technique developed by him and applied to a set of experimental conditions similar to those encountered in the present experimental apparatus were received. (*) Prof. Sparrow has shown that for the following conditions:

$$\text{Surface emittance} = 0.7$$

$$L/R = 10$$

$$T_1/T_0 = 1.15$$

where:

T_1 = temperature at the base of the cavity

T_0 = temperature at the opening of the cavity

L = length of the cavity

R = the radius of the cavity

(*) Private communication

For these conditions the apparent emittance at the base of the cavity is computed to be equal to 0.986. Applying these conditions to the present experimental apparatus and assuming a 4000°F temperature in the bottom of a sight hole, one finds these conditions coincide with a 1200°F per inch temperature gradient, a condition approaching those found in many thermal conductivity measurement runs. This computation again supports the assumption that black body conditions are closely approximated in the sight holes of the experimental apparatus.

2.2 Phase II - Materials Formulations

2.2.1 Metallic Tungsten Systems

The promising results reported during the last quarter on specimens containing metallic radiation reflecting surfaces prompted continued investigation into this composite system. Specimens containing tungsten flake were evaluated in the following runs:

<u>Run No.</u>	<u>% by Weight</u>	<u>% by Volume</u>
34 - 35	30%	1.9
45	25%	1.5
50	20%	1.0
51	20%	1.0

A change in the characteristics of zirconia in a new batch of raw material received during this quarter necessitated process

changes including a significant change in pH in order to develop specimens of similar structure and density to those previously obtained. Unfortunately, these changes also produced specimens of lower strength and lower thermal shock resistance. For this reason several of the thermal conductivity measurements are questionable because of structural failure of the specimens during measurement. In addition, scatter in the data and certain other discrepancies which will be discussed in Section 2.3.2 have necessitated a specimen geometry change which does not allow ready comparison between current and earlier thermal measurements.

Tungsten coated hollow zirconia spheres, described in the previous quarterly report (2) were evaluated in runs 40, 41, 42, 43 and 49. Most of the comments mentioned concerning the tungsten flake specimens also apply to these coated sphere specimens. These data are also discussed in Section 2.3.2.

2.2.2 Molybdate Systems

Two specimens containing molybdenum metal deposited from the decomposition of ammonium molybdate solution were measured in runs 33 and 46. The matrix of the specimen in run 33 was a commercial bubbled alumina material with a relatively large pore structure (over 1000 microns) and yielded erratic results. The specimen of run 46 was a typical zirconia Zr28 type matrix.

2.2.3 Molybdenum Disilicide

Compatibility tests of molybdenum disilicide with zirconium dioxide were run in an oxidizing atmosphere to above the maximum recommended use temperature for molybdenum disilicide. These tests indicate reasonable compatibility between the two materials and therefore zirconia foams containing molybdenum disilicide are being fabricated.

2.3 Experimental Measurements

2.3.1 Thermal Transfer Cell Modifications

The graphite hairpin heater was changed during this quarter after a campaign of 29 excursions to temperatures of over 4000°F. Figure I is a photograph comparing the used graphite hairpin heater with the new one installed during this quarter. It should be stressed that the old heater was still operable and was replaced only because the slight necking down or decrease in cross-sectional area in the hottest zone apparent in the photograph suggested a deviation from the ideal radial heat flow conditions assumed in the thermal conductivity measurements. An increase in the current drawn by the new heater at any given voltage (about 10%) was observed.

The discrepancy in thermal conductivity measurements made in the 1/8" thick gauge section adjacent to the hot face compared with that 3/8" thick gauge section well within the specimen was

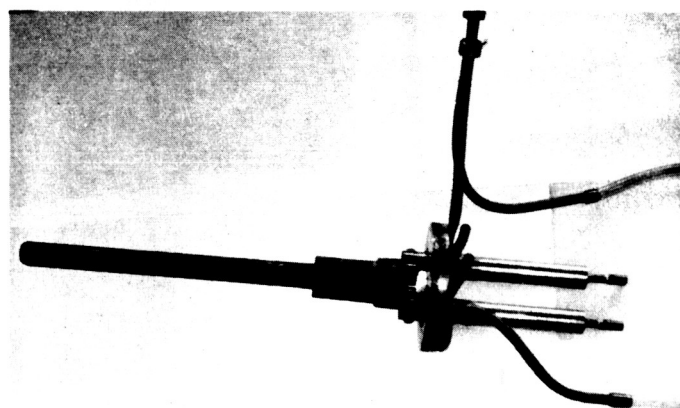
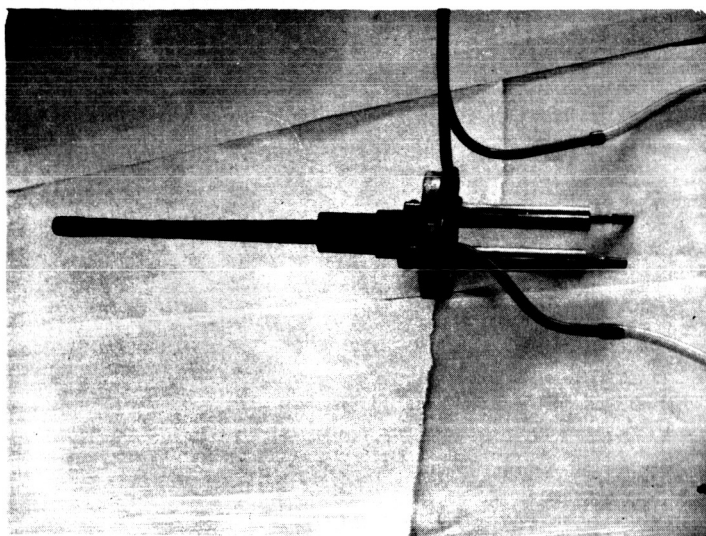


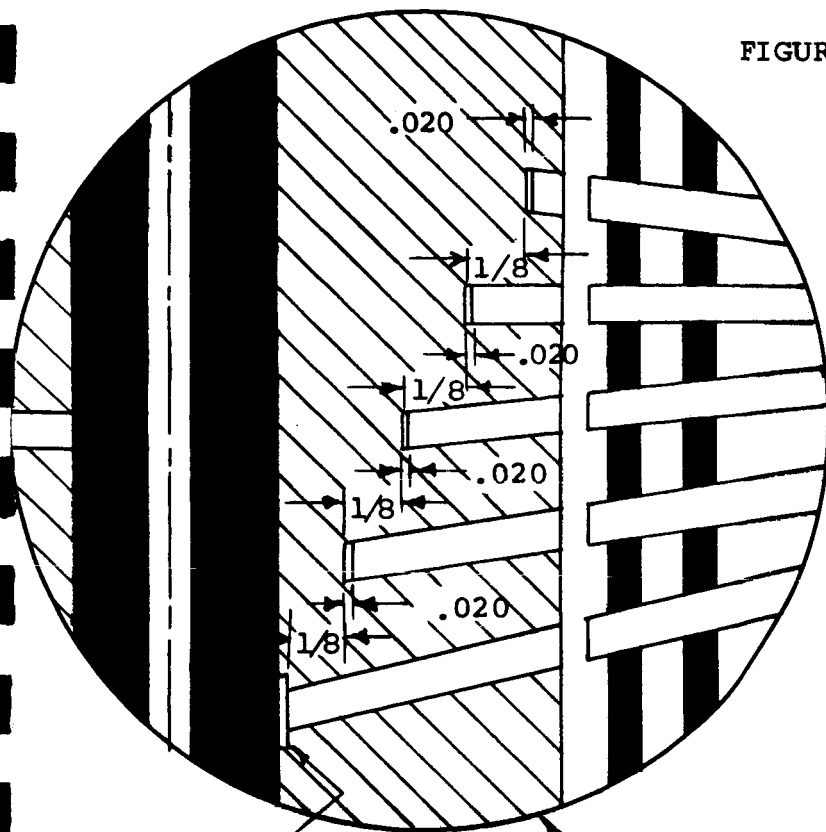
FIGURE 1

Graphite Hairpin Heater Assemblies
Top: After 29 excursions to over 4000°F
Bottom: Unused replacement

discussed in the previous quarterly report. (2) For this reason specimens from run 44 and onward were machined with four gauge sections on each side, each of a 1/8" gauge length. This configuration is shown in the sketch of Figure II. In order to minimize the effect of varying pore size in these porous ceramic foams on the temperature distribution within the samples, a technique of sight hole inserts was developed. Graphite inserts 1/8" dia. by 0.020" thick were machined and placed firmly in the bottoms of sight holes. Temperature measurements made on these graphite inserts were reproducible to a far better extent than those on a porous foam surface. Although the apparent temperature of a sight hole is decreased because of the added interface between specimen and graphite and because of the finite thickness of the graphite, the delta T between any set of holes remains virtually unchanged. A similar technique was tried using circular inserts of molybdenum metal of thickness 0.010". This technique yielded results similar to that of the graphite inserts but fabrication and mechanical placement of these molybdenum inserts was more difficult.

In reviewing the decrease in cross-sectional area of the hairpin heater removed during this quarter it was decided that a monitoring of the uniformity of the temperature distribution

FIGURE 2



.020" GRAPHITE
INSERTS

THROUGH HOLES FOR
HEATER TEMPERATURE
UNIFORMITY
MEASUREMENT

GRAPHITE
HAIRPIN
HEATER

MOLYBDENUM
HEAT SHIELDS

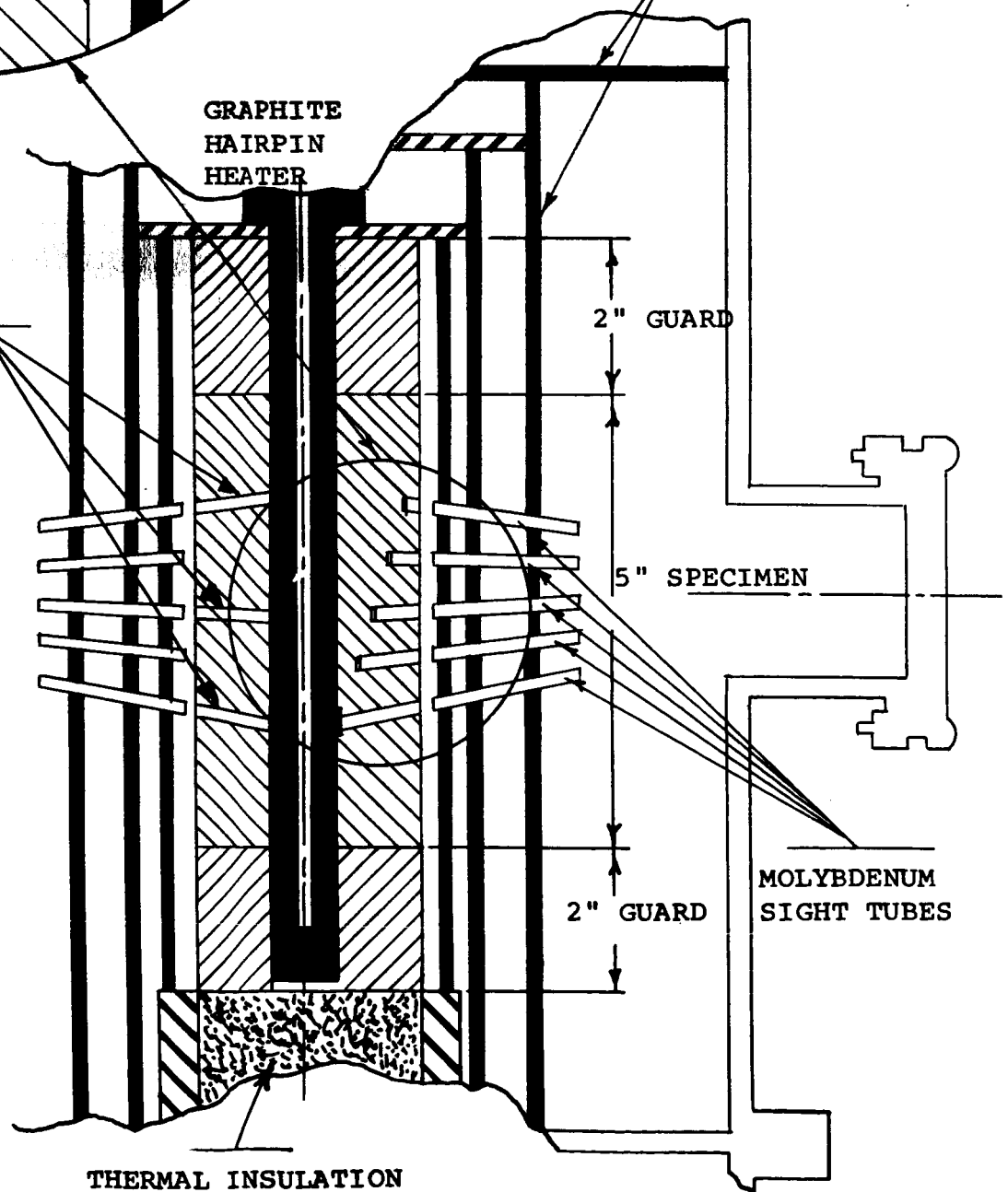
2" GUARD

5" SPECIMEN

2" GUARD

MOLYBDENUM
SIGHT TUBES

THERMAL INSULATION



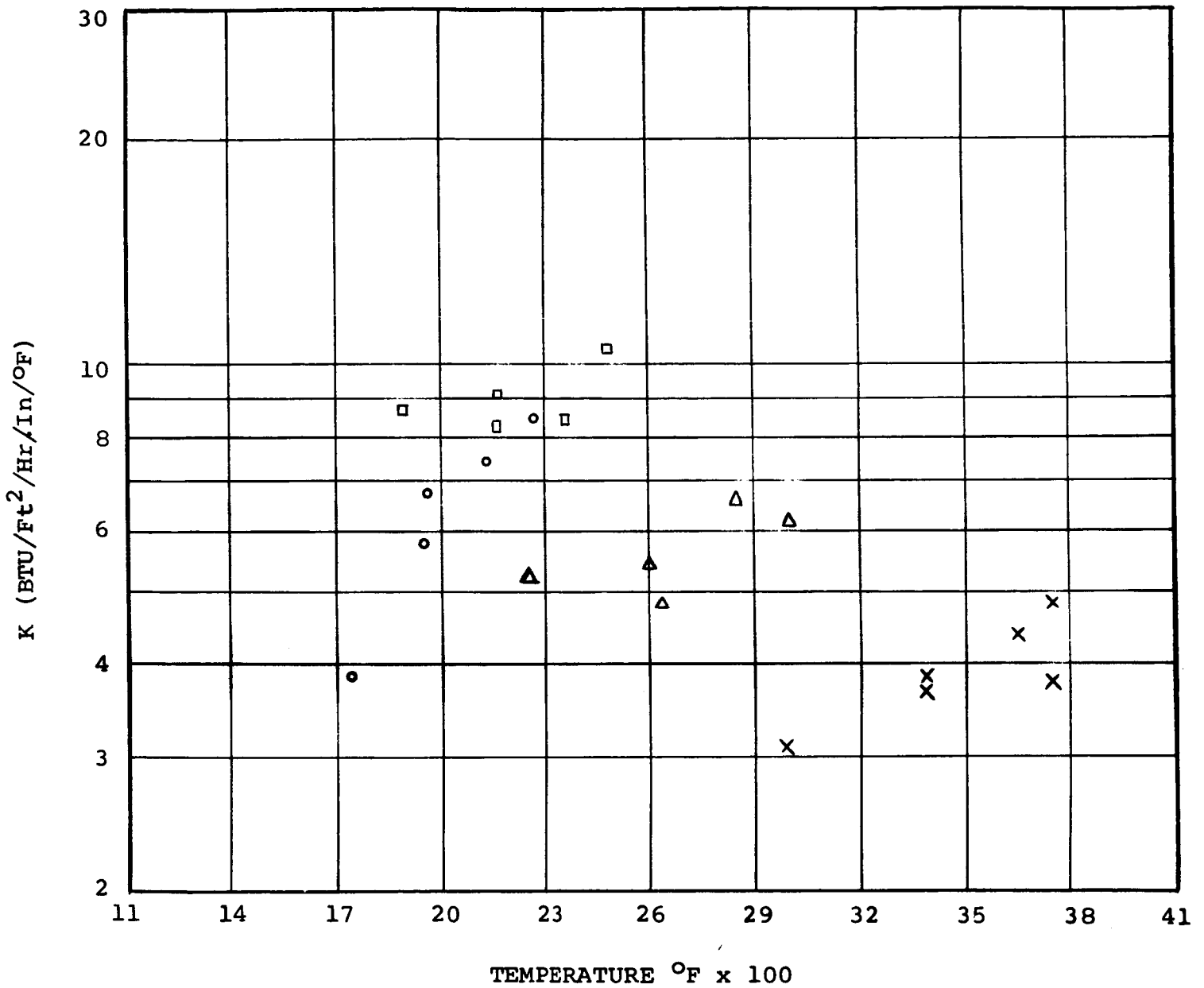
within the specimen was necessary to avoid faulty readings due to inhomogenieties in a specimen. Measurement of the temperature of the heater along several widely separated points was considered advantageous. Since the measurements made in runs 44 through 50 containing the multiple 1/8" gauge sections on each side indicated no differences between the two sides, the policy was adopted of measuring the four gauge sections on one side of the specimen while monitoring the heater temperature over the maximum distance visible from the opposite sight port. This technique allows the hole in the gauge section side previously drilled through to the heater to be filled with a similar graphite insert so that the specimen hot face temperature rather than the heater temperature may be approximated. Data plotted in this manner in run 50 indicate the advantage of this technique.

2.3.2 Conductivity Measurements

Selected thermal conductivity data obtained during this quarter are shown in Figures 3 - 6. Figure 3 is a plot of thermal conductivity vs. temperature for run No. 46. The specimen is type Zr28 zirconia foam impregnated with molybdenum metal by a solution metallizing technique previously described. The added phase of molybdenum metal was measured at 11% by weight after sintering the specimen in hydrogen to 3400°F. The data points of Figure 3 indicate a generally lower thermal conductivity in the hottest sections of the specimen, that is, in the gauge **sections closest to the hot face**. It is apparent that the added molybdenum phase has little effect on thermal conductivity as measured in areas removed from the heat source. Attenuation of the radiation component of thermal conductivity appears to be concentrated in those areas immediately adjacent to the hot face of the specimen. Verification of this observation is required.

The data points of Figure 4 are for run No. 47, in which the specimen was a plain Zr28 type zirconia foam having a density of 0.82 g/cc. A smooth joining of data points is apparent from the gauge sections removed from the hot face, that is, gauge sections 2, 3 and 4. Data points from gauge section 1 are significantly lower due primarily to the measurement of the

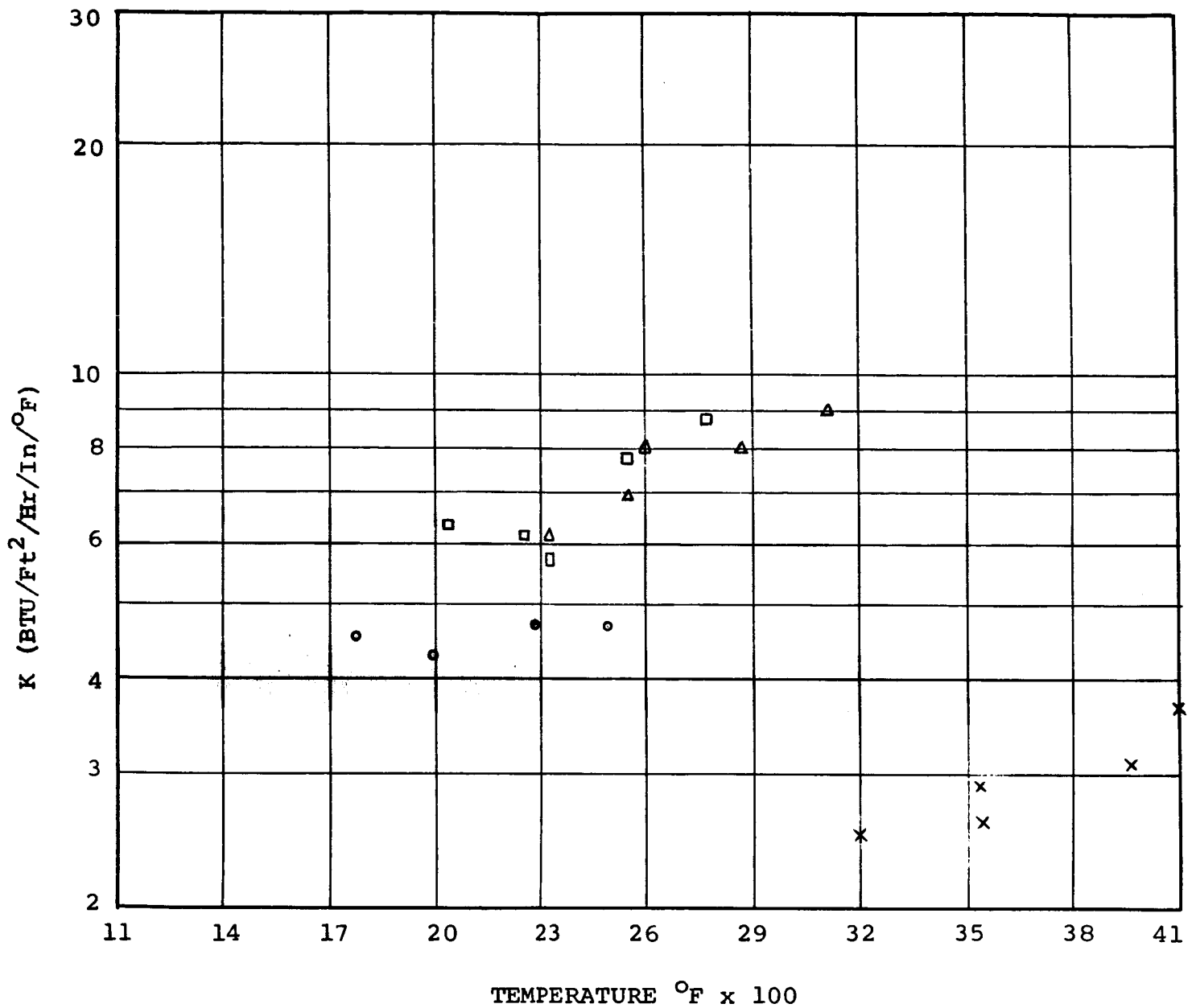
FIGURE 3



- X Gauge Section 1 Adjacent to hot face
- Δ Gauge Section 2 1/8" to 1/4" from hot face
- \square Gauge Section 3 1/4" to 3/8" from hot face
- O Gauge Section 4 3/8" to 1/2" from hot face

THERMAL CONDUCTIVITY VS. TEMPERATURE
Run No. 46

FIGURE 4



- X Gauge Section 1 Adjacent to hot face
- Δ Gauge Section 2 1/8" to 1/4" from hot face
- Gauge Section 3 1/4" to 3/8" from hot face
- O Gauge Section 4 3/8" to 1/2" from hot face

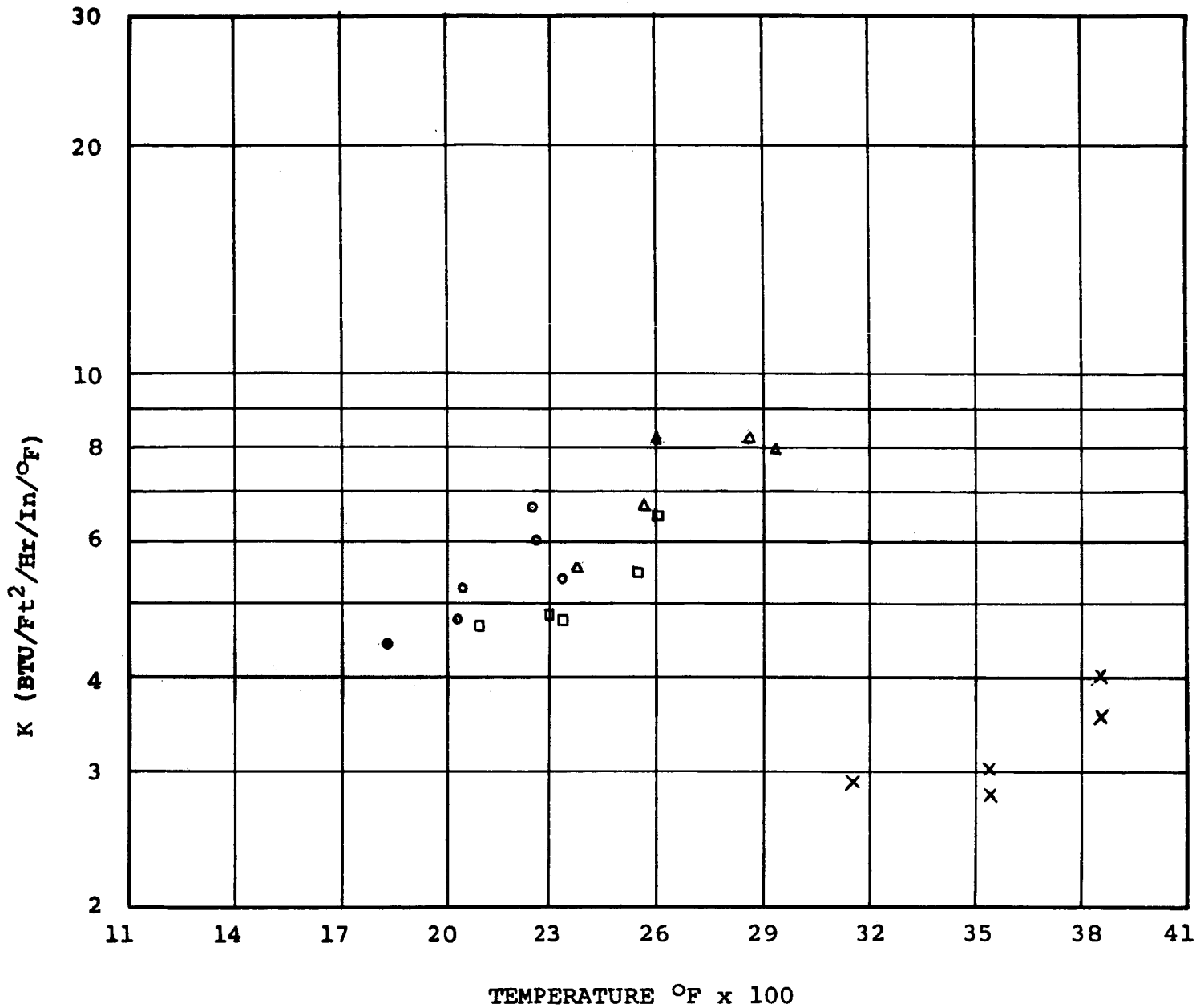
THERMAL CONDUCTIVITY VS. TEMPERATURE
Run No. 47

heater temperature rather than the specimen hot face temperature. The points from gauge sections 2, 3 and 4 agree well with the average of the many points obtained in 3/8" gauge section measurements on similar materials in earlier runs and reported in Figure 4 of the previous quarterly report. Run 47 points are slightly higher in the high temperature range, however, the specimen was slightly more dense than the average of Zr28 type foams previously measured.

Figure 5 is a plot of thermal conductivity data for a specimen of Zr28 type foam of density 0.64 g/cc, but containing 11 percent by weight of tungsten coated hollow zirconia spheres. These spheres, coated with tungsten in a fluidized bed prior to incorporation into the zirconia foam, exhibited a 15 percent by weight pickup of tungsten metal. This corresponds to less than 2 percent by weight tungsten based on the completed composite specimen and is equivalent to less than 0.1 percent by volume of the specimen. The data points indicate that this amount of added tungsten has little significant effect upon the thermal conductivity of the composite. Again, the data points from gauge section 1 are low due to the measurement of the heater temperature.

Figure 6 is a plot of thermal conductivity vs. temperature for run No. 50. The specimen in this case was zirconia foam, type Zr28 with a 19 weight percent addition of tungsten metal.

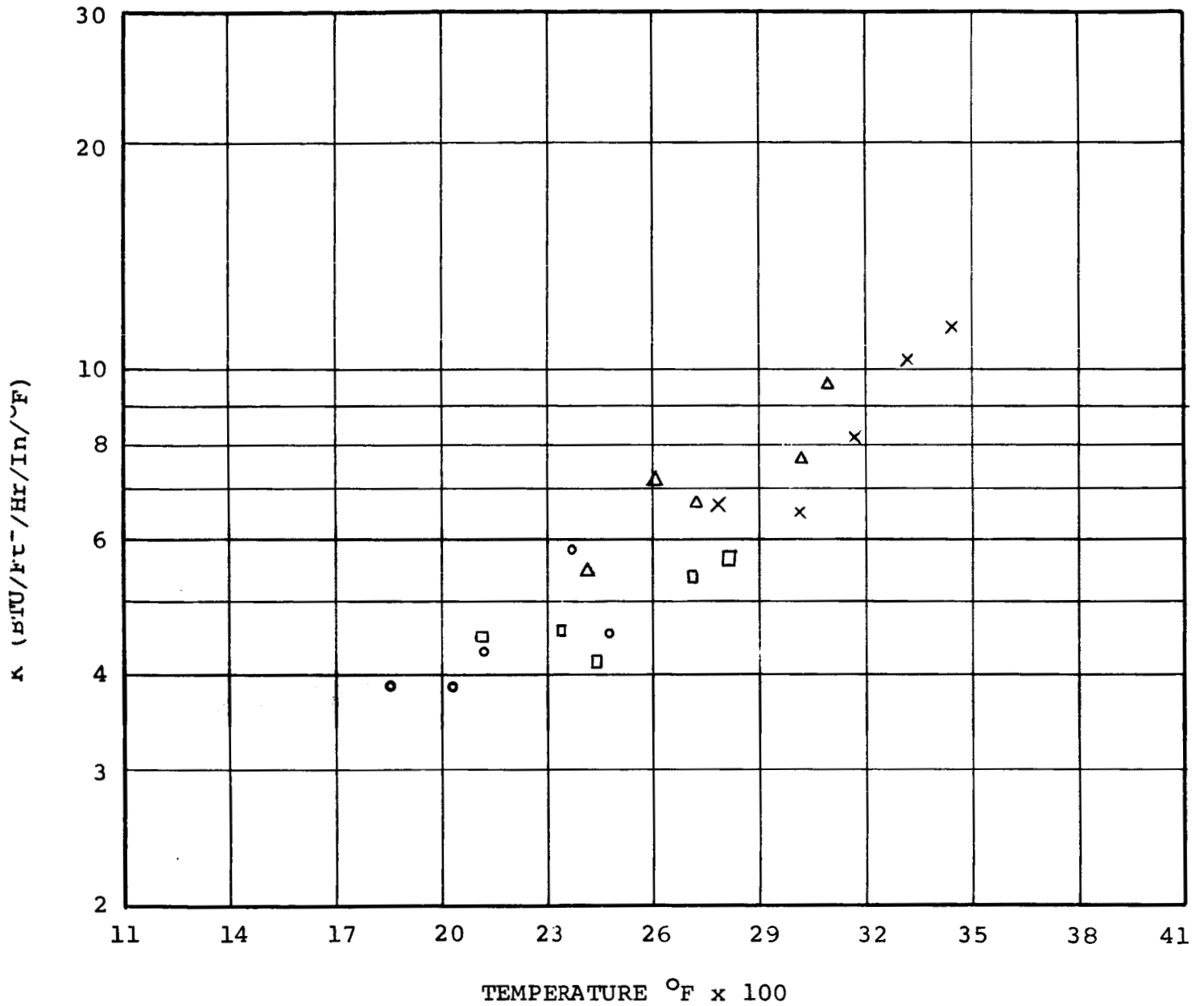
FIGURE 5



- | | | |
|---|-----------------|----------------------------|
| X | Gauge Section 1 | Adjacent to hot face |
| Δ | Gauge Section 2 | 1/8" to 1/4" from hot face |
| □ | Gauge Section 3 | 1/4" to 3/8" from hot face |
| ○ | Gauge Section 4 | 3/8" to 1/2" from hot face |

THERMAL CONDUCTIVITY VS. TEMPERATURE
Run No. 49

FIGURE 6



- | | | |
|---|-----------------|----------------------------|
| X | Gauge Section 1 | Adjacent to hot face |
| Δ | Gauge Section 2 | 1/8" to 1/4" from hot face |
| □ | Gauge Section 3 | 1/4" to 3/8" from hot face |
| O | Gauge Section 4 | 3/8" to 1/2" from hot face |

THERMAL CONDUCTIVITY VS. TEMPERATURE
Run No. 50

The composite specimen had a density of 0.56 g/cc. This specimen was prepared from a new lot of zirconia raw material and exhibited structural weakness and low density, causing an abnormal amount of thermal shock failure during the measurement procedure. Conductivity data are therefore abnormally high. They are included, however, because in this run the technique of graphite inserts in the bottoms of sight holes was extended to the through hole, as shown in Figure 2. This technique allows an estimation of the specimen hot face temperature rather than measuring only the heater temperature. The data points of Figure 6 indicate a reasonably smooth joining of data points from all four of the gauge sections described. This procedure will be considered standard and duplicated in all subsequent runs, including a remeasurement of dense zirconia "standards" obtained in a cooperative measurement program with the Southern Research Institute.

Analytical data obtained on the specimen of run 50 indicate the primary phases present by x-ray diffraction are stabilized cubic zirconia and metallic tungsten with only minor traces of the unstabilized monoclinic zirconia. Comparison with the hot face and cold face surfaces of the composite specimen after measurement shows traces of tungsten carbide only at the cold face surface. Analysis of four different specimens containing

tungsten and two with molybdenum have shown that carbide formation at the hot face is not encountered with either the added metal or from the zirconium oxide.

(3) CONCLUSIONS

Efforts during this quarter have indicated the following:

- (1) Composite specimens containing metallic thermal radiation barrier phases in a zirconia foam matrix are stable to temperatures as high as 2600°C in an atmosphere of purging argon. No reaction is evident between the tungsten or molybdenum and the zirconia nor between the graphite heater and either of these components.
- (2) A modified thermal conductivity measurement technique employing four gage sections, each 0.125" long extended from the hot face of the specimen through a ½" depth normal to the heat flow has been developed. A technique of employing thin graphite inserts in specimen sight holes to establish uniform isotherms in a porous foam specimen has been evaluated and found useful in diminishing scatter in measured data points.
- (3) There is substantial evidence that added metallic thermal radiation barrier phases effectively attenuate high temperature thermal conductivity. Measurements in gauge sections removed from the specimen hot face indicate little effect at distances greater than 0.250". The attenuation of the radiation component of thermal conductivity appears to be concentrated in a skin depth section less than 0.250" from the hot face. The magnitude and depth of this phenomena is yet to be evaluated.

(4) PROGRAM FOR NEXT QUARTER

Fabrication and testing of zirconia foam samples containing various thermal radiation barrier phases will continue. Emphasis will be centered upon specimens containing tungsten flake and particulate molybdenum particles by solution metallizing technique. Specimens containing molybdenum disilicide will also be evaluated.

A recalibration of the thermal conductivity apparatus will be made using a "standard" of dense zirconia previously measured on equipment at the Southern Research Institute. In this manner the multiple gauge section technique may be directly compared with other techniques developed in other laboratories.

Efforts will be made to determine the extent and location of the attenuation of the radiation component of thermal conductivity in the skin areas adjacent to the hot face of ceramic foam composite materials.

REFERENCES

1. Sparrow, E. M., "Radiant Emission, Absorption and Transmission Characteristics of Cavities and Passages", Symposium on Thermal Radiation of Solids, San Francisco, California, March 4, 1964.
2. Styhr, K. H., et al, "Research on Low Density Thermal Insulation Materials for Use Above 3000°F", Seventh Quarterly Status Report, Contract NASr-99.